AIRBORNE CONCENTRATIONS OF POLYBROMINATED DIPHENYL ETHERS IN PRIVATE CARS

Hazrati S[1], Harrad S.[2], Mokhtari A.[1], Rahimzadeh F.[3]

[1] Department of Environmental Health, Ardabil University of Medical Science, Ardabil, Iran
[2] Division of Environmental Health and Risk Management, University of Birmingham, Birmingham, UK, B15 2TT
[3] Education Office of Tehran Province, Tehran, Iran

Abstract

Airborne concentrations of PBDEs were investigated using PUF disk passive air samplers in 25 private cars. ΣPBDE concentrations ranged between 0.01 and 8.2 ng m^{-3} with respective arithmetic and geometric mean concentrations of 0.71 and 1.87 ng m^{-3}. High concentrations of PBDEs found in cars might provide an important source of human exposure to PBDEs either via inhalation or dust ingestion. Excluding two most contaminated cars, linear regression revealed a significant positive relationship ($p<0.01$) between log-normalised PBDE concentrations and vehicle age. To explain wide variation in airborne concentrations of PBDEs between cars from same manufacturer with similar ages, further monitoring of PBDE contamination in cars is warrant. The median ratio of BDE 47:99 for air samples was 1.7 comparing with the respective values of ~1 and ~0.7 reported for BK 70-5DE and DE-71, suggesting these commercial formulations to be likely sources of PBDEs in the car indoor environments.

Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of organic compounds widely detected in all environmental compartments as a result of their intense industrial and commercial applications[1-5]. While generally their ambient concentrations in air and water are not considered to exert severe direct hazards via inhalation and ingestion, respectively; their hydrophobicity`, combined with their resistance to degradation via mechanisms like photolysis, hydroxyl radical attack and biological action has resulted in global dispersion of PBDEs and subsequently biomagnification in terrestrial, freshwater aquatic and pelagic food chains. Owing to their thermal stability, high bromine content (good flame retardant properties), and relatively low costs, PBDEs are used as flame-retardant additives (i.e. they are only dissolved in the material) in order to reduce fire hazards by interfering with the combustion of the polymeric materials [6]. They are also added to wires and cables, textiles, polyurethane foam, carpets and upholstery used in household and business furnishings, cars, buses, trucks, and aircraft [7]. Although PBDEs are ubiquitous environmental contaminant, however, less is known about it's concentrations in car indoor microenvironments. In order to characterize airborne concentrations of PBDE in indoor microenvironments and their possible sources, this study monitored PBDEs levels in 25 private cars in the West Midlands, UK using passive air sampling technique.

Material and Methods

Sample collection: PUF disk passive samplers were used to collect air samples. A total of 25 private cars from variety of marques and makes were selected and PUF disk passive samplers were located on the cradle and fixed inside car boots for a period of 4-6 weeks. Sampling rate (SR) of PUF disk samplers obtained employing a calibration campaign using a low volume active air sampler [8]. Congener based sampling rates were applied to estimate ambient concentrations of 7 BDE congeners. Passive sampling rates for the 7 PBDE congeners monitored showed relatively low variability (RSD = 17.6%) varying from 1.12 (BDE 99) to 1.94 m^3 day^{-1} (BDE 47), therefore, a sampling rate of 1.64 m^3 day^{-1} based on average of SR values determined for PBDEs 17, 28, 47, 49, 66, 99, and 100 was applied to estimate airborne concentrations for other PBDEs.

Sample preparation and analysis: PUF disks were treated with 10 ng of PBDE surrogate standards (ISs including PBDE #s: 28, 47, 99, and 153) prior to extraction in a pre-cleaned 200 ml soxhlet apparatus for 8 h using HPLC grade hexane. The crude extract was concentrated to approximately 2 mL, treated with 2 mL concentrated sulphuric acid, prior to elution through a column containing one gram Florisil (Aldrich Chemicals; 60–120 mesh, pesticide grade). Analyses were conducted on a Fisons' MD-800 GC/MS system fitted with a 60 m VF5 MS column.

QA and QC measures: The precision of passive sampling and analytical procedures combined was evaluated by simultaneously deploying 5 passive samplers in a temporarily vacant domestic microenvironment for 6 weeks. Average relative standard deviations (RSD) between the 5 replicate analyses for the PBDE congeners was 17%. To determine the accuracy and precision of the analytical protocol, 5 replicate aliquots of SRM 1944 (New York/ New Jersey Waterway Sediment) were analysed for PBDEs throughout the study.

Results and discussions

Concentrations of PBDE in indoor air: ΣPBDE refers to the sum of the BDE #s 17, 28, 47, 49, 66, 85, 99, 100, 153, and 154. ΣPBDE concentrations in private cars varied from 0.01 to 8.2 ng m^{-3} with respective arithmetic and geometric mean concentrations of 0.71 and 1.87 ng m^{-3} (Table 1).

Table 1:Summary of indoor air concentrations of PBDEs (pg m^{-3}) in this study and worldwide

Indoor microenvironment	average	Min	Max
Homes and offices[9]	1800	60	15500
Homes[10]	260	2	3600
Homes[11]	15		
Offices[11]	30		
Offices[12]	205*		
Homes[12]	8*		
Cars[13]		0.4	2644
Windscreen Film[14]		280000	1772000
Cars	709	11	8184

* Geometric means

ΣPBDE concentrations in this study are similar to those reported for other indoor microenvironments where ΣPBDE concentrations were found to be in range of 0.06-15.5 ngm^{-3} [9, 13]. However, our findings are much higher than the concentrations reported by other studies in which PUF disks were employed to monitor indoor air concentrations of PBDEs in residential indoor environments [10-11].

Although human intakes occur principally through dust ingestion and dietary pathways, significant variations in concentrations of PBDEs in ambient indoor air, means that inhalation exposure may be far more significant for some people. For instance, assuming an inhalation rate of 20 m^3 day^{-1} for an adult, a taxi driver spending 8 hours daily in a contaminated car would receive a daily inhalation exposure of 54 ng.

Factors influencing PBDE concentrations: Amongst the many potentially important factors influencing PBDE concentrations, the age and manufacturer of cars were studied. The age of the cars varied from 2 to 21 years and vehicles from 12 different manufacturers were monitored. Linear regression of log-normalised ΣPBDE concentrations in all monitored cars with vehicle age revealed no statistically significant relationship ($R = 0.291$; $p = 0.16$). When two of the most contaminated cars were excluded as outliers, a significant ($p<0.01$) positive linear relationship was detected between PBDE concentrations and vehicle age.

Although the limited number of samples taken from each marque precludes the drawing of any firm conclusions as to whether cars made by different manufacturers vary in contamination levels, the average ΣPBDE concentrations are compared within the cars from different manufacturers in Table 2.

Airborne concentrations of PBDEs in some cases varied by more than 2 orders of magnitude between cars from the same manufacturer (i.e. for Nissans between 11 and 2571 ng m^{-3}). Since the cars were similar in age, thus it does not appear to be due to variations in vehicle age, and instead may be the result of differences in the quantity and type of PBDE-containing goods such as electronic equipment. However, more data are required to characterise PBDE emission sources in cars and this area warrants further research.

Table 2: Indoor air and windscreen film concentrations of BDE in cars of different manufacturers

	[a] Indoor air concentrations (pg m^{-3})			[b] Windscreen Film (µg m^{-2})
	Number	Average	SD	Average
VW	2	25	18	Na
Honda	1	30		0.351
Mazda	1	36		Na
Mercedes	1	42		1.772
Fiat	3	62 (23-89) [c]	35	Na
Toyota	3	155	221	0.323
Ford	1	177		0.28
Renault	3	271 (20-752)	417	Na
Nissan	5	538 (11 – 2571)	1137	Na
Peugeot	2	2356	3241	Na
Rover	2	4253	5559	Na
other	2	18		Na

[a] This study
[b] From Gearhart and Posselt (2006)
[c] Range of PBDE concentrations and Na is not available

PBDE sources in indoor microenvironments

As previously stated, tri- to hexa-brominated diphenyl ethers were monitored in this study, which covers the majority of the congeners present in the most pertinent formulations to be produced or used in the UK (i.e. penta BDE commercial formulations). Congener profiles of PBDEs in cars were compared with the congener composition of the two penta BDE formulations principally employed in the UK; namely DE-71 and Bromkal 70-5DE. For this purpose, the concentration ratios of BDE 47 relative to BDE 99 in cars along with those in commercial penta-BDE formulations are provided in Table 3.

For all air samples the median ratio of BDE 47:99 is 1.7, which is comparable with the respective values of ~1 and ~0.7 reported for BK 70-5DE and DE-71, suggesting these commercial formulations are likely sources of PBDEs in the indoor environments studied. These relatively higher BDE 47:99 ratios in car microenvironments, supports the hypothesis that preferential volatile emissions of the lower brominated 47 c.f. 99 from household items favour higher ratios in air compared to those detected in the treated material itself.

Ratio of BDE 47:99 in ambient air and commercial mixtures

	Mean	SD	Median	
Car	1.7	0.92	1.7	This study
Indoor air [10]	3.8			Wilford et al. (2004)
Indoor air [11]	2.4			Gevao et al. (2006a)
Indoor air [9]	5.3	3.01		Harrad et al. (2004)
BK 70-5DE[15]	1			Sjodin et al. (1998)
DE-71 [16]	0.69			Hoh and Hites (2005)

References:

1. Abraham K., Hille A., Ende M. and Helge H. (1994) *Chemosphere* 29; 2279.
2. Koopmanesseboom C., Huisman M., Weisglaskuperus N., Vanderpaauw C. G., Tuinstra L., Boersma E. R. and Sauer, P. J. J. (1994) *Chemosphere* 28;1721.
3. Bencko V., Cerna M., Jech L.and Smid J. (2004) *Environ Sci Technol* 18 ;83.
4. Jones-Otazo H. A., Clarke J. P., Diamond M. L., Archbold J. A., Ferguson G., Harner T., Richardson G. M., Ryan J. J. and Wilford, B. (2005) *Environ Sci Technol* 39; 5121.
5. Harrad, S., Hazrati, S., and Ibarra, C., (2006).Concentrations of polychlorinated biphenyls in indoor air and polybrominated diphenyl ethers in indoor air and dust in Birmingham, United Kingdom: implications for human exposure. *Environ Sci Technol* 40; 4633.
6. Rahman F., Langford K. H., Scrimshaw M. D., Lester J. N. (2001) *Science of the Total Environment*, 275, 1-17.
7. WHO (World Health Organization) (1994) IPCS. *Environmental Health Criteria* (EHC)162, Geneva.
8. Hazrati S. and Harrad S. (2007) *Chemosphere*, 67; 448.
9. Harrad S., Wijesekera R., Hunter S., Halliwell C. and Baker R. (2004) *Environ Sci Technol* 38; 2345.

10. Wilford B. H., Harner T., Zhu J. P., Shoeib M. and Jones, K. C. (2004) *Environ Sci Technol* 38; 5312.
11. Gevao B., Al-Bahloul M., Al-Ghadban A. N., Ali L., Al-Omair A., Helaleh M., Al-Matrouk K. and Zafar J. (2006) *Atmospheric Environment* 40; 1419.
12. Mandalakis M., Atsarou V. and Stephanou E. G. (2008) *Environmental Pollution* 155; 375.
13. Mandalakis M., Stephanou E. G., Horii Y. and Kannan K., (2008) *Environ. Sci. Technol*. 42**;** 6431.
14. Gearhart J. and Posselt H. (2006) available on line at www.ecocenter.org, accessed on 12/04/2006.
15. Sjodin A., Jakobsson E., Kierkegaard A., Marsh G., and Sellstrom, U. (1998) *Journal of Chromatography A* 822; 83.
16. Hoh E. and Hites R. A. (2005) *Environ Sci Technol* 39; 7794.